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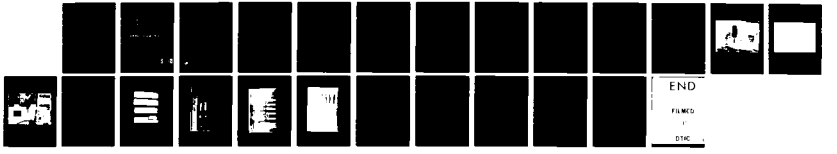

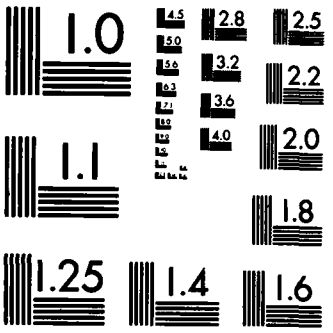

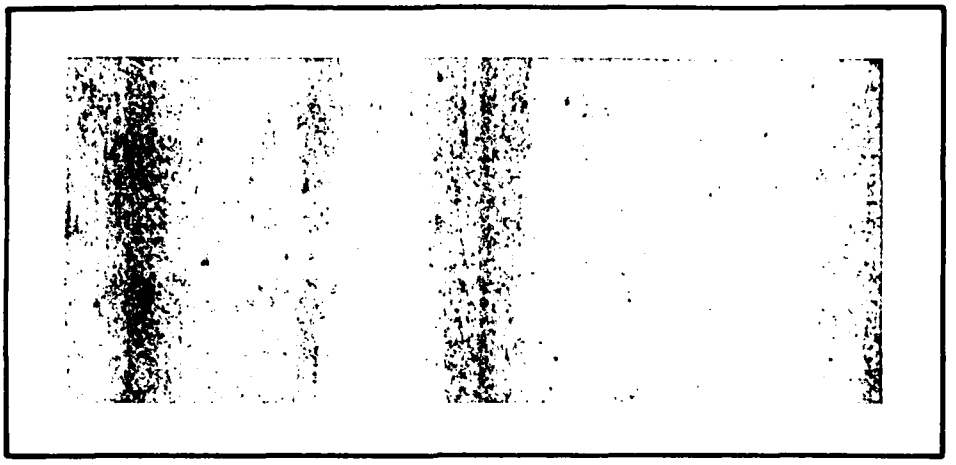

SCIENCE APPLICATIONS, INC.

SAI Report No.
SAI-018-82-064LJ

MEASUREMENT OF OXYGEN CONTAMINATION IN TITANIUM ALLOY INGOTS BY FAST NEUTRON ACTIVATION ANALYSIS

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Final Report

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1.0 INTRODUCTION

This final technical report describes the progress made at Science Applications, Inc., in demonstrating a capability to measure the total oxygen content of titanium alloy using nondestructive nuclear techniques.

The oxidation of titanium alloys, caused by interstitial oxygen contamination is a serious problem that causes metal fatigue. Should the welding process of a titanium alloy be interrupted, oxygen from air can get into the weld area and start the oxidation process. Hence, it is important to be able to certify, with high degree of certainty, the assurance of the noncontamination of a weld area with oxygen, and to point out the region of the welds which do not meet the desired specifications. The method used should meet the following criteria:

1. Nondestructive
2. Quantitative
3. Reliable
4. In-Process
5. Fast
6. Safe
7. Cost-Efffective

While other efforts related to this measurement determine changes in electrical resistivity, transit time of shock wave transmission, or thermoelectric currents, etc., due to increase or decrease in oxygen content of titanium alloy, they do not produce absolute values of oxygen. False measurements, due to some unknown factor related to changes in crystalline structure of titanium alloy, can result if some of the previously mentioned techniques are used. However, the nuclear technique probes into the very structure of matter, inducing nuclear transformation of oxygen atoms and signaling, with gamma-ray emission, their absence or presence in the metal analyzed. The activation analysis of oxygen with 14 MeV neutrons is a well established and validated analytical technique; it is a rare example of an analytical method that is virtually free of interferences and gamma-ray attenuation effects that utilizes short-lived isotopes, thus permitting a very rapid analysis.

In this report, the determination of oxygen content of titanium alloy - 6211 - will be demonstrated with a great deal of accuracy and reliability. The ultimate goal is to develop a safe and reliable portable unit that can measure oxygen levels in titanium or metallic welds, and indicate whether to accept such a weld or reject it based on its oxygen content.

2.0 SURVEY OF LITERATURE

Fast neutron activation analysis has proven to be a highly sensitive and precise method for bulk oxygen measurement (1-4). The technique is based on inducing a nuclear transformation of the oxygen atoms in the matrix by the use of $^{16}O(n,p)^{16}N$ reaction initiated by a flux of 14 MeV neutrons. Blake et al [5] utilized this technique to measure oxygen contamination in high-purity beryllium samples and were able to detect 20 parts per million (ppm) oxygen in specimens analyzed. Vogt and Ehmann, [6] determined non-destructively the level of oxygen in meteorites using fast neutron activation to [7]Word et al, used fast neutron activation analysis to determine the oxygen content of steel samples and were able to perform 600 measurements per day with a detection limit of 10 ppm. Wood and Pasztor [8] used fast neutron activation analysis to determine oxygen in steel samples, compared the results with those obtained using vacuum fusion techniques, and concluded that nuclear methods were much faster and more reliable than conventional methods.

Bryne et al,[9] devised an automatic system to determine oxygen in beryllium metal components that weight 500-2000 gms, using fast neutron activation techniques. Their results compared favorably with those obtained with existing chemical methods.

3.0 THEORY OF ACTIVATION ANALYSIS

Neutron activation analysis is a nuclear method for quantitative elemental analysis. It is a sensitive, accurate and reliable analytical technique. It involves the irradiation of a sample with neutrons from a nuclear reactor or fast neutron generator, then measuring the intensity of the characteristic gamma-rays emitted by the produced radioactive atoms. The elemental composition of the sample is obtained by comparing the intensities of the gamma-rays emitted by the sample to the intensities of the gamma-rays emitted by irradiated elemental standards. The measurement of gamma-rays is accomplished by using a high-resolution Ge(Li), or NaI(TL) detector coupled with a gamma-ray spectrometer.

The determination of oxygen by fast neutron activation makes use of the $^{16}O(n,p)^{16}N$ nuclear reaction initiated by a flux of 14 MeV neutrons. The unstable ^{16}N nucleus, formed in the reaction, decays with a half-life of 7.3 seconds and emits gamma-rays of 6.1 and 7.1 MeV of energy.

These gamma-rays are detected by a NaI(TL) detector and their number is proportional to the oxygen content of the irradiated specimen. The governing equation for fast neutron activation analysis:

$$D = \frac{Nf\,\sigma\,\varepsilon}{\lambda}(1-e^{-\lambda t_b})\,(e^{-\lambda t_w})\,(1-e^{-\lambda t_c}) \qquad (1)$$

where

- D = counts recorded by the detector
- N = the number of nuclei in a sample which can undergo a given reaction
- f = the neutron flux (neutron/cm^2/sec)
- σ = the isotopic reaction cross section
- ε = the efficiency of the radiation detection including geometric factors
- λ = the decay constant of the radioactivity produced
- t_b = duration of neutron bombardment
- t_w = arbitrary waiting time
- t_c = arbitrary counting time

Comparison of the gamma-ray yield obtained from a sample to that obtained from a reference standard, provides a measure of the oxygen content of the sample as stated by the following relationship:

$$\frac{\text{counts of sample}}{\text{counts of standard}} = \frac{\text{weight of oxygen in sample}}{\text{weight of oxygen in standard}} \qquad (2)$$

The fast neutron generator is actually a deutron accelerator used to produce 14 MeV neutrons by means of the $^{3}He(d,n)^{4}He$ nuclear reaction. It is a commercially available unit with accelerating energies of 100-600 KeV and a deutron beam of 1-5 milliamps and a total neutron output of 10^{9}-10^{11} n/second.

As 14 MeV neutrons interact with other components of the Ti-alloy such as V or Nb, any produced gamma-ray has much lower energy than 6.1 MeV produced by ^{16}N. Lower gamma-ray energies are not counted and are discriminated against in the single channel gamma-ray spectrometer. The presence of elemental fluorine in the matrix can produce ^{16}N by the nuclear reaction of $^{19}F(n,\alpha)^{16}N$. The probability of interaction for this reaction is low and if the ratio of oxygen to fluorine is 10:1, the error produced is 5%. It is very unlikely for flourine to be present in any significant level in titanium, or metals in general, to cause any serious errors to the oxygen measurements.

4.0 EXPERIMENTAL

4.1 Instrumentation

The fast neutron generator available to SAI is a product of Kaman Science, Inc. (Fig 1). It produces a total of 10^{11} n/sec in 4π geometry or a neutron flux of 10^{8} n/cm^2/sec at the sample's irradiation position. The system is equipped with a dual automatic counting and transfer system (Fig 2). Samples to be irradiated are encapsulated in 3 1/2" x 3/4" polyethylene, which are sent by pressurized air to the irradiation position in the generator. The gamma-ray counting setup (Fig 3) consists of two 4" x 4" NaI(TL) detectors in a lead shield connected separately to a single-channel analyzer and a total count printer. Counts of both sample and standard are printed out after each irradiation. The fast Neutron generator is shielded with concrete to prevent fast neutrons from reaching operating personnel.

4.2 Procedure

A - SAMPLE AND STANDARD PREPARATION

SAI received fire titanium bars of alloy 6211 (Fig 4). The bars had dimensions of 1" x 1" x 6" and were numbered as follows:

NRL-A-5-1
NRL-B-5-1
NRL-C-5-1
NRL-D-5-1

Each of these titanium alloy bars were fabricated into five cylinders, each of which had 0.79 cm diameters and a length of 3.75 cm. Extreme care was exercised in the machine shop to prevent the mixing of the different titanium alloys. In order to remove any possible surface contamination, each fabricated titanium cylinder was washed with the following reagents in this numerical order:

1. carbon tetrachloride
2. reagent-grade acetone
3. distilled deionized water
4. concentrated nitric and hydroflouric acid mixture 4:1

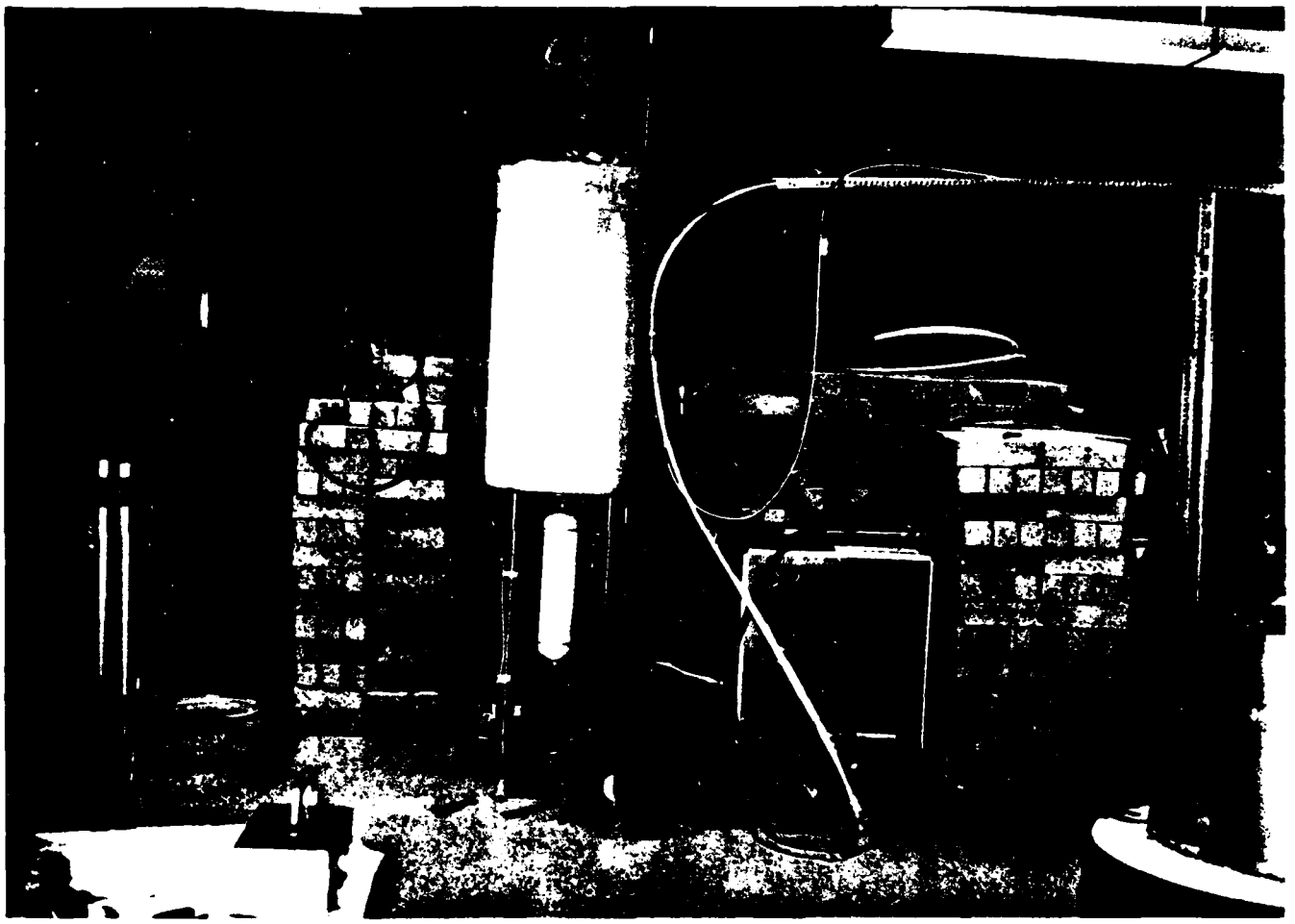

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Figure 1. Fast Neutron Generator.

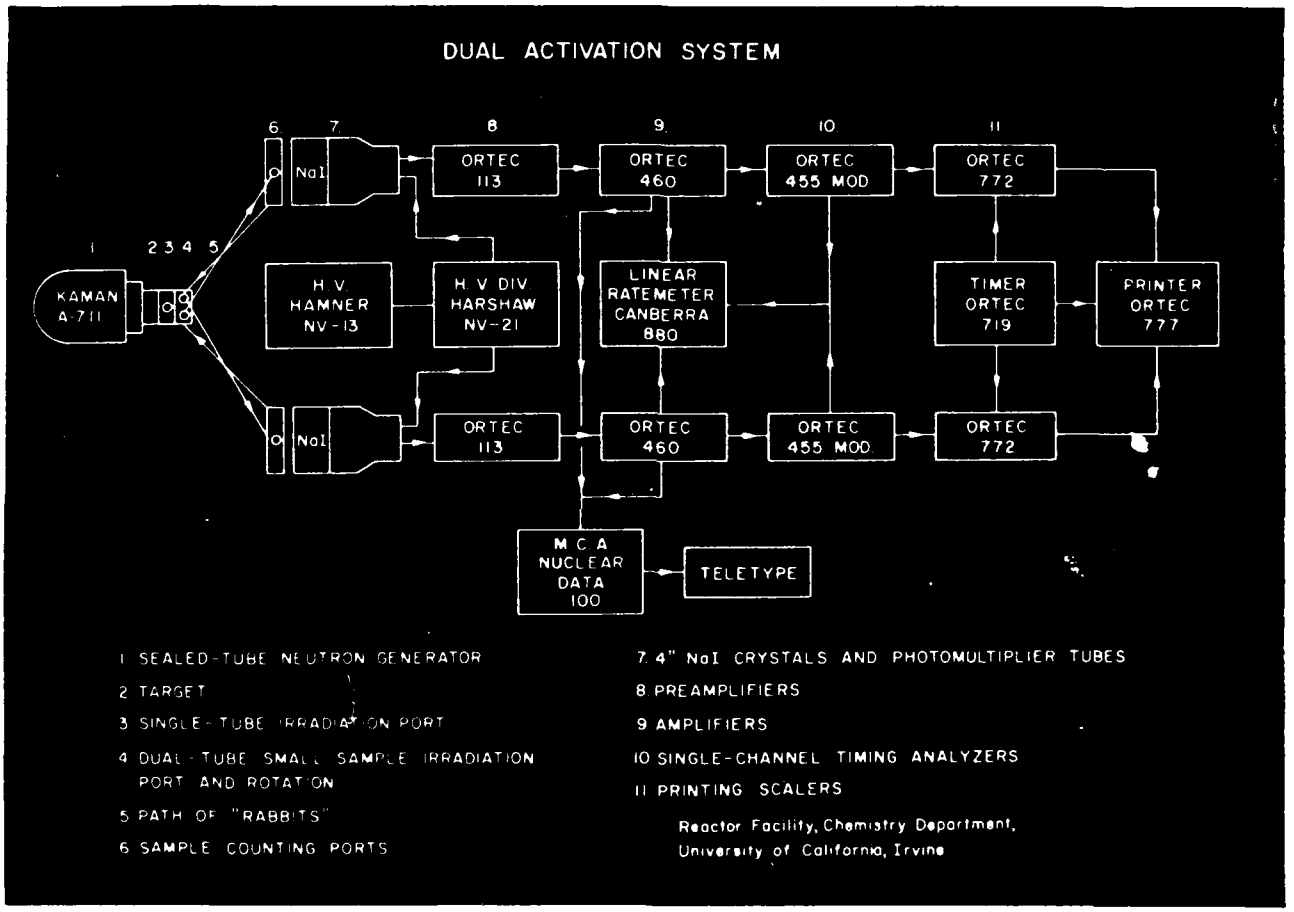

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Figure 2. Dual Activation and Transfer System.

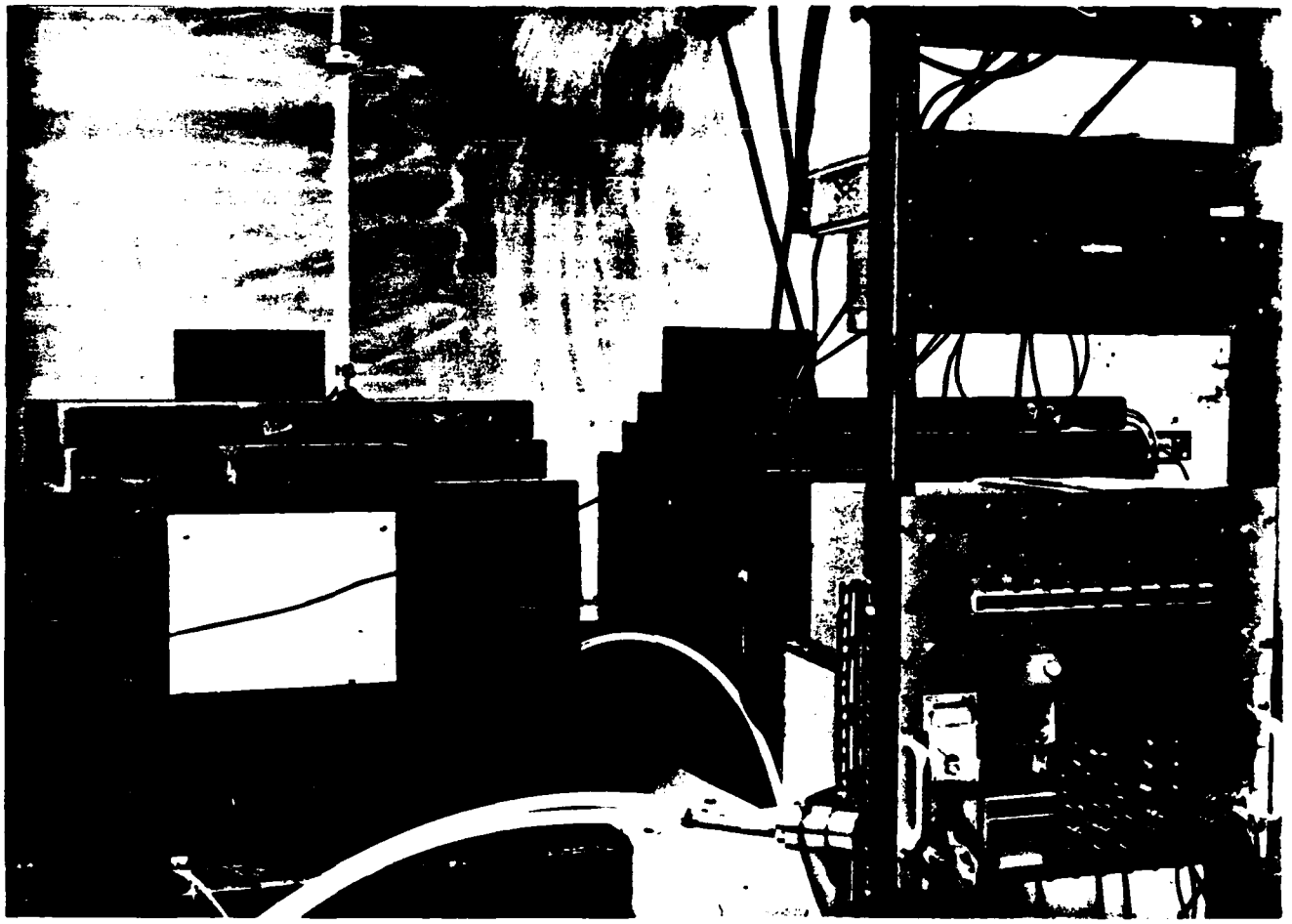

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Figure 3. Gamma-Ray Counting System.

5. distilled deionized water
6. reagent-grade acetone
7. dried with heat lamp

It was then encapsulated and heat sealed in 1 3/4" x 3/4" polyethylene irradiation vials as shown in Figure 5, 6. Five oxygen standards were prepared by filling each polyethylene irradiation vial with two grams of benzoic acid of known oxygen content and sealing them. Blanks (empty polyethylene irradiation vials) were prepared by flushing them with nitrogen gas and heat sealing them. (Fig. 7)

B - IRRADIATION AND COUNTING

Titanium alloy samples and benzoic acid standards were transferred together by pressurized air to the irradiation position in the fast neutron generator. They were irradiated for 20 seconds at a flux of 1×10^8 $n/cm^2/sec$. During irradiation, they were rotated along their axis to receive a hemogeneous exposure of neutrons.

After irradiation, they were allowed to decay for 3 seconds and were transferred by pressurized air into two separate NaI(TL) gamma-ray detectors, each connected to a single-channel gamma-ray analyzer and a line printer.

Each sample and standard were counted for 20 seconds. The counds, due to oxgyen activation in the titanium alloy and oxygen activation of the benzoic acid standard, were recorded on two separate printers. The operation of irradiating and counting was repeated several times on each sample in order to get a good replication of results.

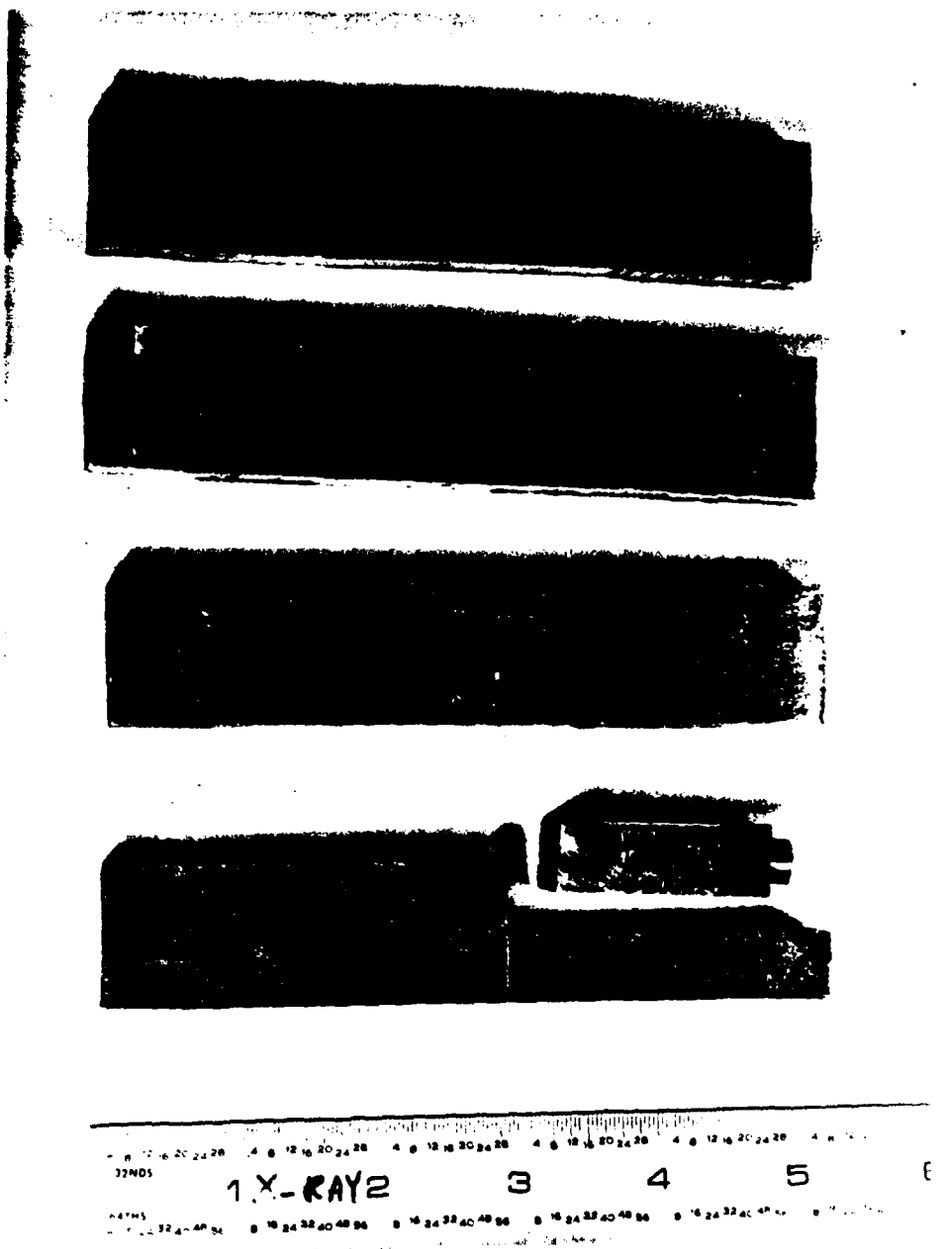

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Figure 4. Titanium Alloy-6211.

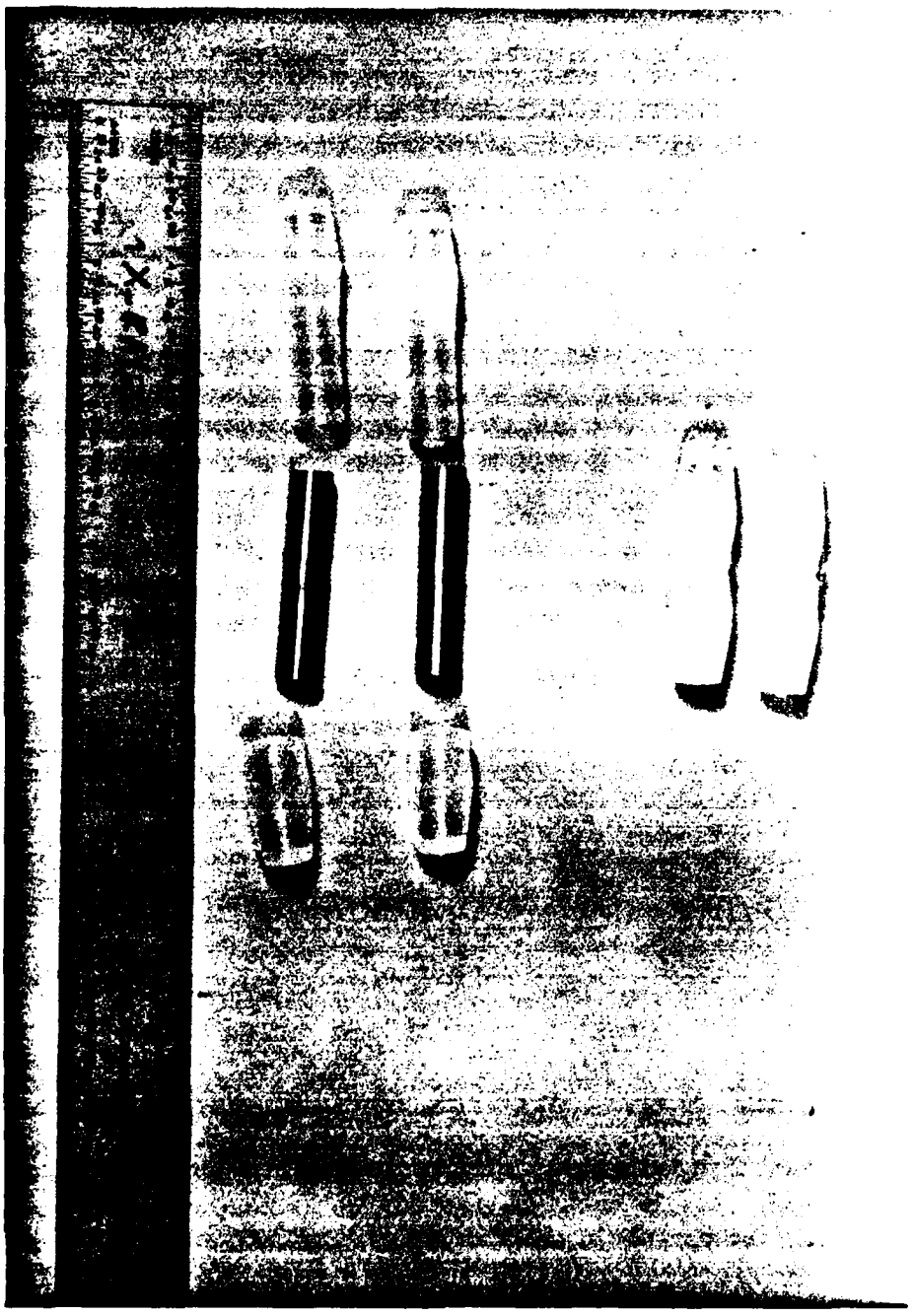

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Figure 5. Irradiation Capsul

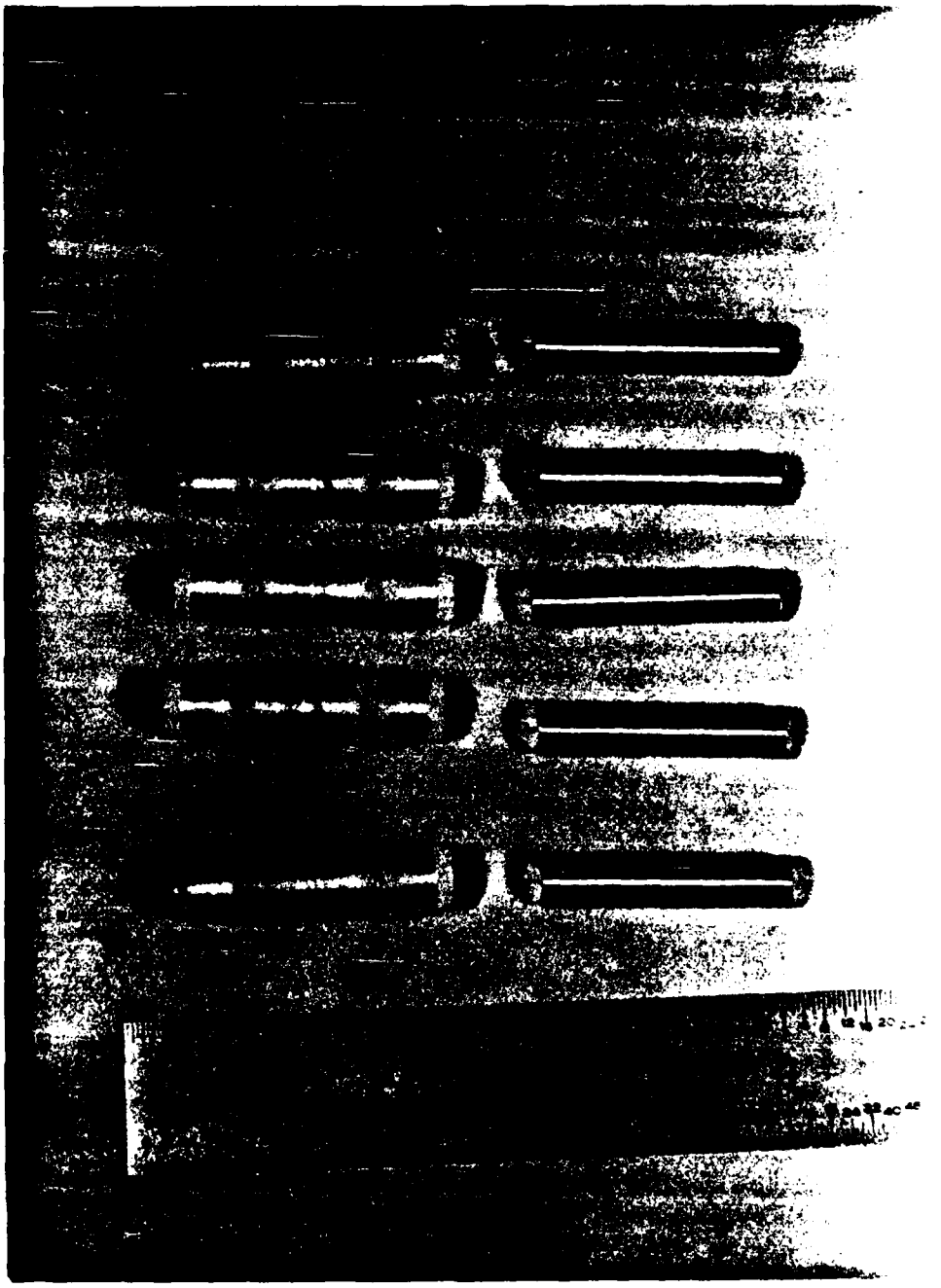

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Figure 6. Titanium Alloy in Irradiation Capsul

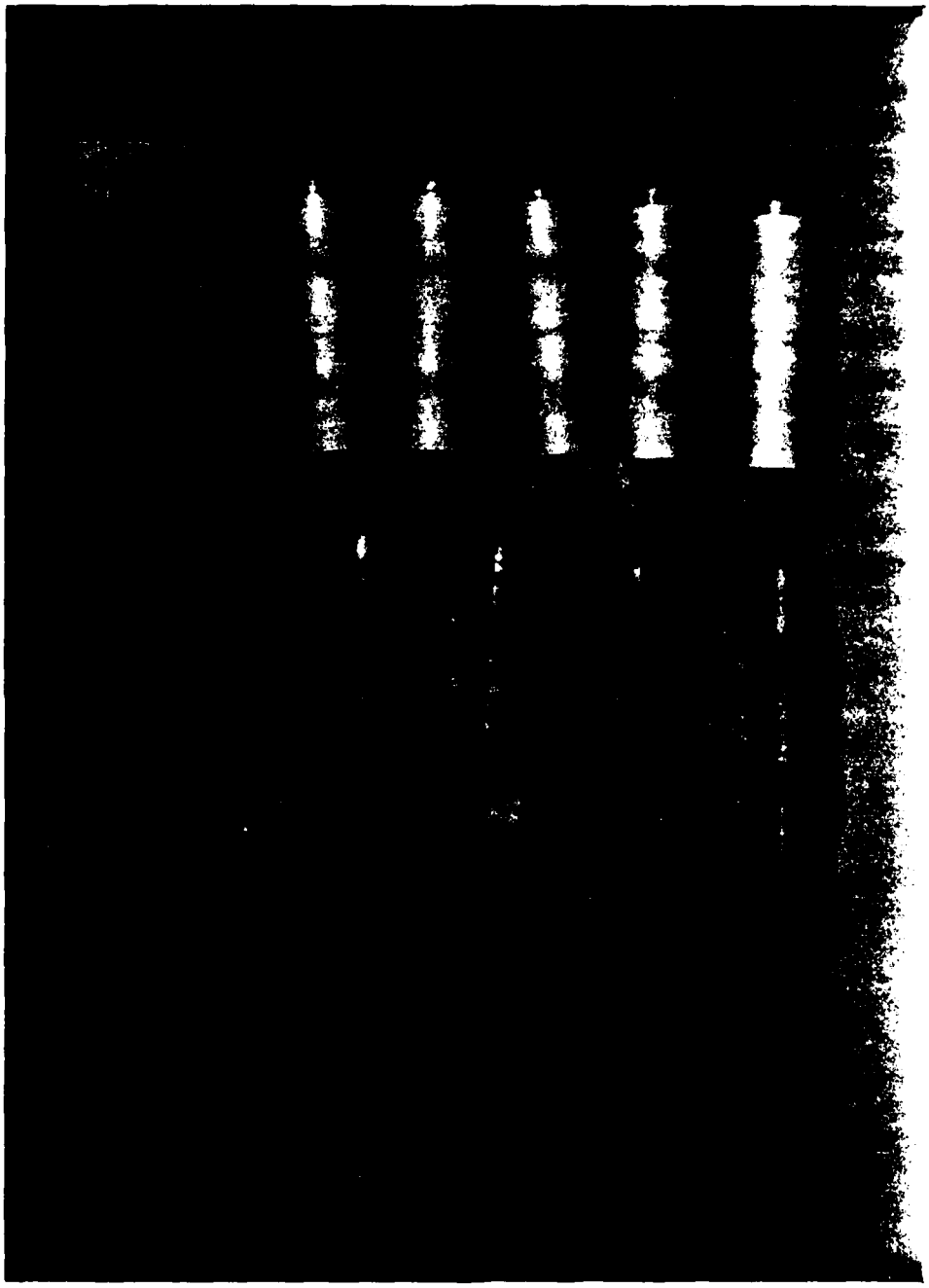

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Figure 7. Oxygen Standards of Benzonic Acid.

5.0 EVALUATION OF RESULTS

Knowing the oxygen content, and the count rate in the benzoic acid standards, and the count rate of each irradiated titanium cylinder, the mass of oxygen in each irradiated titanium cylinder was calculated. Table (1) shows a very good replication of the percentage of oxygen in each titanium cylinder analyzed. Table (2) shows the average oxygen content of five replicates from each of titanium bar A, B, C, D, and E. The relative error in these determinations is small and ranges between 2.8% and 3.9%.

More confidence in the accuracy of the oxygen values obtained by fast neutron activation is derived when the obtained results agree very well with those obtained by R.M.I., Inc. using vacuum fusion, Table (2). A correlation coefficient of 0.994 between the two sets of independent oxygen analysis is obtained. Furthermore, when 1 gm of H_2O sample was analyzed by fast neutron activiation using benzoric acid as standards, water was experimentally found to contain 89.36% oxygen while theoretically it contains 88.88%.

SAMPLE		% OXYGEN		σ
A_1	=	0.0661 %	±	0.0013
A_2	=	0.0708 %	±	0.0011
A_3	=	0.0667 %	±	0.0014
A_4	=	0.0674 %	±	0.0015
A_5	=	0.0668 %	±	0.0014
Average = 0.0675 % ± 2.8 %				
B_1	=	0.125	±	0.0016
B_2	=	0.125	±	0.0020
B_3	=	0.126	±	0.0036
B_4	=	0.126	±	0.0021
B_5	=	0.134	±	0.0034
Average = 0.127 % ± 3.0%				
C_1	=	0.160	±	0.0027
C_2	=	0.167	±	0.0029
C_3	=	0.170	±	0.0027
C_4	=	0.168	±	0.0022
C_5	=	0.161	±	0.0019
Average = 0.165 ± 2.7 %				
D_1	=	0.226	±	0.0061
D_2	=	0.234	±	0.0041
D_3	=	0.235	±	0.0017
D_4	=	0.239	±	0.0041
D_5	=	0.224	±	0.0041
Average = 0.231 % ± 2.7 %				
E_1	=	0.253	±	0.0034
E_2	=	0.268	±	0.0028
E_3	=	0.278	±	0.0022
E_4	=	0.278	±	0.0047
E_5	=	0.275	±	0.0038
Average 0.270 % ± 3.9%				

TABLE 1 Oxygen Content of Ti-6211

SAMPLE		NAA MEASURED % OXYGEN		RELATIVE ERROR	VACUUM FUSION % OXYGEN
NRL-A-5-1	=	0.0675	±	2.8 %	0.075
NRL-B-5-1	=	0.127	±	3.0 %	0.136
NRL-C-5-1	=	0.165	±	2.7 %	0.194
NRL-D-5-1	=	0.231	±	2.7 %	0.238
NRL-E-5-1	=	0.270	±	3.9 %	0.290

Correlation Coefficient = 0.994

Slope = 1.038

Intercept = 0.0081

TABLE 2 Agreement of Oxygen Values Produced By NAAI with Those by Vacuum Fusion

6.0 CONCLUSION

It can be concluded from this study that fast neutron activation analysis provides a nondestructive analysis for oxygen content in titanium alloys. This analysis proved to be intereference-free, to reach parts per million sensitivity, and to provide fast, accurate, and reliable results.

7.0 BIBLIOGRAPHY

1. S. S. Nargolwalla, E. P. Przybylowicz, Activation Analysis with Neutron Generators, Wiley, New York, 1973.

2. D. E. Wood, Nucl. Instr. Methods, 92 (1971).

3. R. L. Schulte, E. A. Kamykowski, J. of Radioanalytical Chem., 43 (1978) 233.

4. S. S. Nargolwalla, E. P. Przybylowicz, J. E. Suddueth, and S. L. Birkhead, Modern Trends in Activation Analysis (1968), NBS S. P. 312, p. 879.

5. Blake, K. R. ; Martin, T. C.; Morgan, I. L.; Houston C. D., Measurement of Contamination of High-Purity Beryllium Samples. Proceedings of International Conference on Modern Trends in Activation Analysis, pp 76-81, (1965).

6. Vogt, J. R. and Ehman, W. D., "Nondestructive Determination of Silicon and Oxygen in Meteorites by Fast-Neutron Activation Analysis". Proceedings of the International conference on Modern Trends in Activation Analysis, pp 82-85, (1965).

7. Wood, J. D.; Downton, D. W.; and Blake, J. M., "Fast-Neutron Activation Analysis System with Industrial Applications." Proceedings of the International Conference on Modern Trends in Activation Analysis, pp 175-181, (1965).

8. Wood, P. E. and Paztor, L. C. "A Comparison of Neutron-Activation Analysis and Vacuum-Fusion Analysis of the Oxygen Content of Steel". Proceedings of the International Conference on Modern Trends in Activation Analysis, pp 259-264, (1965).

9. Bryne, J. T.; Illslay, C. T. and Price, H. J., "An Automatic System for the Determination of Oxygen in Beryllium Metal Components". Proceedings of the International Conference on Modern Trends in Activation Analysis, pp 304-309, April (1965).